U. S. Department of Agriculture, Forest Service

FOREST PRODUCTS LABORATORY

In cooperation with the University of Wisconsin

MADISON, WISCONSIN

THE LEACHING OF ZINC CHLORIDE FROM TREATED WOOD

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Approved Copy Filed
10-9-19

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In the treatment of wood with inorganic salts as a wood preservative, the most important factor which controls the length of life of the preservative is its permanence in the wood in a toxic condition. There are three methods by which the toxic effect of inorganic salts may be reduced. These are -

1. Leaching of the salt with water, thus removing considerable portions of the preservative from the wood.

2. Loss of salt by volatilization.

3. Decomposition of the salt with the removal of the toxic ion by leaching or with the removal of the non toxic ion in such a manner as to leave the toxic ion bound up in an insoluble form and hence non toxic.

All of these conditions are known to take place in actual practice.

Of the three methods, the second that of volatilization is of the least importance in inorganic salts because as a rule such salts are not volatile. The only commercial inorganic preservative which is effected in this manner is mercuric chloride and in this case the disappearance of the toxic effect may be due to a combination of both the second and third methods, that is actual loss by volatilization and decomposition from the mercuric to the mercurous salt. In practice the greatest stress is

usually laid on leaching of the preservative and the possibility of decomposition seems to have been nearly forgotten. That this method of failure of the preservative is important is shown by the failure of wood treated with a solution of calcium cresylate. When this salt is exposed to the atmosphere, calcium carbonate is formed and cresol is obtained in a free condition, this being both volatile and soluble in water soon disappears from the wood.

On account of the prominence given to the leaching of a preservative, several processes have been patented to overcome this undesirable feature in the treatment with zinc chloride, such as the Wellhouse process and B.M. Preservative. One of the tests used at the Forest Products Laboratory to determine the efficiency of a wood preservative is the ease with which inorganic salts leach from wood. These tests are carried out by treating sections of noble fir 2x2x18 with a solution of the various salts and then cutting each section into three pieces 2x2x6; each piece was then submerged in water for a period of 28 days, the water being changed from time to time. The solutions were then analyzed for their content of preservative and the loss by leaching calculated in percentage of the total amount in the piece. The results of these tests seem to indicate that under this method of testing all inorganic salts leach at about the same rate. Calculations show

that with the exception of perhaps sodium fluoride, all woods treated with a preservative would have enough moisture in it under normal conditions (air dry) to keep any commercial treatment of salts in solution. If this is the case, then the relative leaching of any salt will not be dependent upon the solubility unless a saturated solution is used, but will depend upon the rate of diffusion and probably upon the species of wood used.

Leaching of Zinc Chloride

Zinc chloride is now and has been for some years the most important inorganic wood preservative in commercial use. In the past several small samples of rotten wood have been received at the laboratory which on analysis were found to contain a very high per cent of zinc. This led us to believe that the zinc must have been rendered non toxic and it seems probable that this might have been due to the hydrolysis of the zinc chloride. It is well known that on dilution of solutions of zinc chloride, a precipitation of basic zinc chloride takes place in general agreement with the equation 3 $ZnCl_2$ plus $2H_2O$ =4H Cl plus $Zn_3O_2Cl_2$, or some other basic chloride of the same general formula so that it seems likely that some such a reaction may take place in the wood during service. Eventually all of the zinc left in the wood would be in the form of a basic chloride, so insoluble that it should not have a very toxic

effect. If this hypothesis is correct, we ought to be able to get a measure of this action by a careful determination of both the zinc and chlorine which is leached out of wood by a leaching method. The following experimental work was undertaken along the lines suggested.[1]

Experimental

Nine matched pieces of clear hemlock 8x1-3/4x2" were treated for one-half hour under 120 lbs. pressure at 60°C. with a one, three, and five per cent solution of zinc chloride. The pieces were then dried somewhat in the air. The solutions used were made up from a concentrated solution of anhydrous zinc chloride in water by diluting to the proper density. They were then filtered and analyzed for both zinc and chlorine by the usual volumetric methods. The results of these analyses are given in Table I.

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[1] This work was done in this laboratory by Mr. C. A. Fourness and submitted to the University of Wisconsin as his Bachelor's thesis.

Table I.-Concentration of treating solutions

Concentration of $ZnCl_2$ sol.	Zinc mg. per cc.	Chlorine mg. per cc.	Excess Chlorine over required amt. for $ZnCl_2$ mg. per cc.	Per Cent Excess Chlorine	Concentration of solution in HCl
1.00%	4.79	5.44	.24	4.58	.024%
2.87%	13.74	15.38	.48	3.22	.049%
4.85%	23.25	25.89	.67	2.66	.069%

After drying five days the wood was placed in wide-mouthed glass stoppered jars and submerged in 1300 to 1400 cc. of water. The water was changed in the following intervals:

Leach No.	Time of Leaching
1	30 minutes
2	1 day
3	2 days
4	2 days
5	3 days
6	7 days
7	7 days
8	7 days
Total time	29 days

The volumes of the solutions were carefully determined and then analyzed for both chlorine and zinc. After leaching, the wood was dried in the oven and completely reduced to sawdust and analyzed for zinc. At that time no

method of analysis of the wood for chlorine was available so the assumption was made that the chlorine entered into the wood in the same relative proportion to the zinc as was found in the treating solution. The results obtained were then calculated to a percentage basis and plotted in the form of curves. (Figs. 1, 2).

<u>Discussion of Results</u>

The curves show that that the chlorine leached out at a greater rate than the zinc. In Figure 1 the actual amounts of zinc and chlorine leached were 6.429 gms. zinc and 9.879 gms. chlorine. This is 3.092 gms. chlorine over that required for the $ZnCl_2$ leached and 2.67 gms. chlorine in excess when the original acidity of the solution is taken into account, similarly the figures for the stick nearest the average in the other two solutions are 3.81 gms. and 6.17 gms. chlorine in excess of $ZnCl_2$ and 3.10 and 5.19 gms. chlorine in excess when calculated back to the original acidity. It is very evident from the above that the chlorine leached more rapidly than the zinc. This is to be expected when we consider the fact that $ZnCl_2$ hydrolyzes with the formation of basic chlorides. The basic chlorides are indefinite compounds being limited on one end by $ZnCl_2$ and the other by ZnO.

The rate of leaching should be governed by the rate of diffusion of the salt used and possibly by some

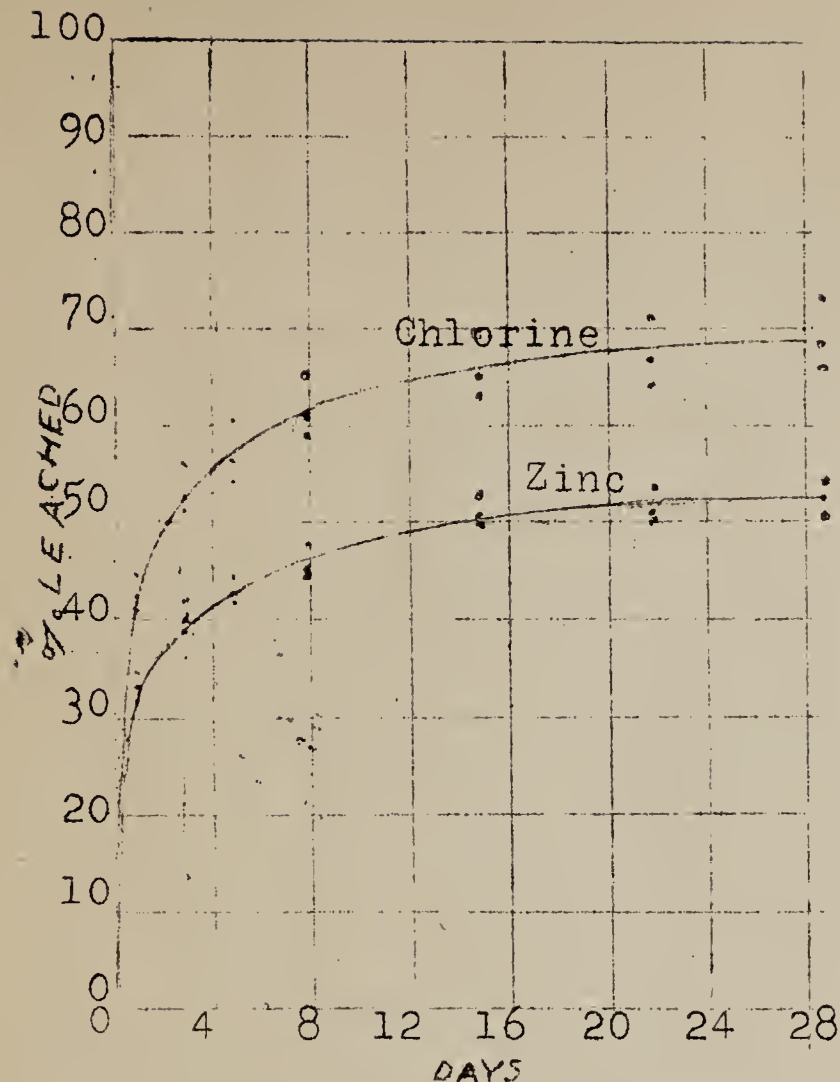

Fig. 1

Leaching of Zinc and Chlorine from Wood Treated with One Per Cent Solution of Zinc Chloride

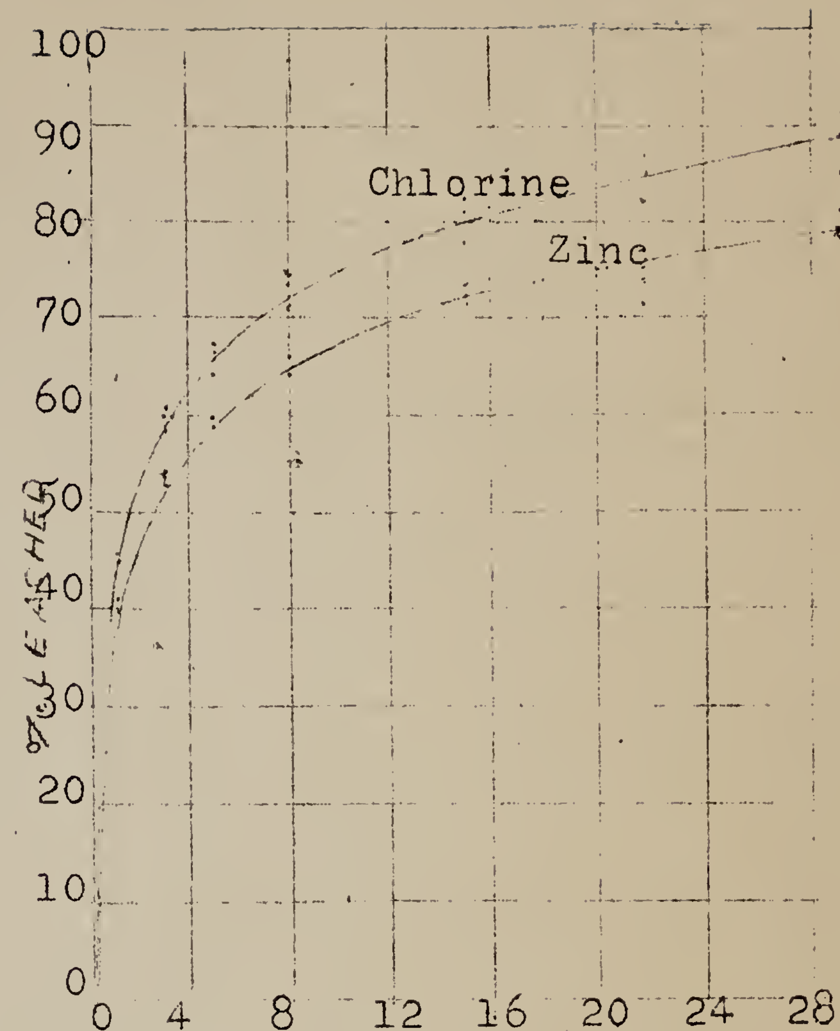

Fig. 2

Leaching of Zinc and Chlorine from Wood Treated with 4.85 Per Cent Solution of Zinc Chloride

(Figures based on the amount of zinc and chlorine injected)

constant for the species of wood. If this is so, we ought to be able to calculate the amount of $ZnCl_2$ and HCl which would be leached, provided we know the rate of diffusion of the zinc chloride and hydrochloric acid. The value of the diffusion constant K of hydrochloric acid as given by Thovert[2] at 192°C. and .02 mols per L is 2.12. No values are available for $ZnCl_2$ but it is known that in general the chlorides diffuse faster than the sulphates. Thovert gives the value K for .55 mols $ZnSO_4$ per liter at 19.5°C. as .36 so that if we estimate this value as .5 for zinc chloride we will probably be not far off from the truth. Using these values for K and calculating the amounts of zinc chloride and HCl which would diffuse for a 5% solution in increments of 1 gm. zinc chloride leached, we find that for 4 gms. of zinc chloride to diffuse from 100 cc. of 5% solution requires the diffusion of .26 gms. HCl and the precipitation of .603 gms. of zinc chloride, if we assume that the composition of the basic zinc chloride is $ZnCl_2.5ZnO$ (Perrot). When this is calculated to a percentage basis and we take into consideration the excess acid originally present we find that in order to diffuse 80% of the zinc that 88.2% of the chlorine should also diffuse. Practically we obtained 89 per cent. This is a very fair agreement with the theoretical value and

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[2] Landolt - Bornstein, Physikalisch Chemische Tabellen.

seems to indicate that the leaching of salts from wood under the conditions of the experiment is probably a diffusion phenomenon and consequently we should be able to foretell the rate of leaching of other salts from wood if we know the rate of diffusion in water and the constant for the species.

Leaching of Zinc Chloride under Practical Conditions

It is of interest to apply this idea to the disappearance of zinc chloride from treated wood and to determine if the same effect takes place in actual service as is shown to have taken place in the laboratory. Most, if not all wood treated with zinc chloride, is in the form of railroad ties. The condition of leaching here is somewhat different from that in the leaching experiments described above. In the laboratory experiments the leaching out of the salt was continuous; in service we have the following conditions. During wet weather leaching takes place with the result that basic zinc chloride is deposited in the tie. During dry weather, moisture is evaporated, thus concentrating the solution, particularly near the surface. In concentration, the free hydrochloric acid necessary to maintain an equilibrium at the lower concentration is now more than sufficient at the higher concentration. This excess acid is either taken up by redissolving any basic chloride which may be

present or may be lost during the process of evaporation. We might expect, therefore, a result similar to that obtained by straight leaching with water, but requiring longer time to accomplish the same degree of leaching.

Analysis of Ties Treated with $ZnCl_2$

Description of Ties

In 1918 it was found necessary to remove on account of splitting, tie No. 319 of the Hartford test track on the Chicago, Milwaukee and St. Paul Railroad. This tie was one of a number treated at this laboratory in cooperation with the above railroad and placed in their track in August, 1911 for service test. The tie, although it was removed on account of splitting was nevertheless decayed and two sections were sent to the laboratory for analysis. The following is the treating record of this tie:

Species	Treatment	Sapwood per cent	Absorption per cent dry salt lbs. per cu. ft.
Hard Maple	Burnett[3]	89.4	.61

[3] The Burnett treatment consists of a single injection with a solution of zinc chloride.

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The results of the analyses of these ties proved to be of such interest that it was decided to corroborate the findings by other samples. Accordingly in June, 1919, during the inspection of the test track of the Chicago and Northwestern near Janesville, Wisconsin, ten other samples were taken. The condition of the time was not such as to warrant their removal but in several places they were split for one reason or another and where the split portion was not sustaining any of the burden, these portions were removed. These ties were treated experimentally by the Forest Service in cooperation with the Chicago and Northwestern Railroad at Escanaba, Michigan. They were laid in the track in December, 1909. We have no individual treating record on them but only an average of the lot treated at one time. The description of the sample is given in Table II.

Method of Examination

The method of sampling each section of tie No. 319 is shown in Plate I as well as a description of the physical condition of each portion taken for analysis. The specific gravity of each portion was determined. It was then reduced to sawdust and thoroughly shaken to ensure a fair sample. Separate samples were then taken for the zinc and chlorine determinations. For the most part

Table II.- Description of samples taken from Chicago and Northwestern test track

Tie No.	Species	Process used in treatment	No. of ties in treatment	Average absorption	Portion taken as sample	Remarks
200	Peeled hemlock	Well-house	40	0.43	Splinter 1"x 3"x18" above ground; from end of tie	Entirely sound. Rest of tie sound but bruised at end
313	Peeled hemlock	Well-house	40	0.39	Splinter 1"x 3"x30" above ground; rail to center	Sample sound. Small decayed portion under sample. Rest of tie sound
486	Peeled tamarack	Burnett	125	0.43	Splinter 3/4"x 2"x24"; from center of tie above ground	Sample sound, broken off by bruise. Rest of tie sound
527	Peeled tamarack	Burnett	125	0.43	Splinter 1"x 4"x18"; from end to rail	Sample slightly decayed. Rest of tie decayed near split.
657	Unpeeled tamarack	Burnett	125	0.51	Splinter 3/4"x 2½"x18"; from end to rail	Sample sound. Rest of tie sound
752	Unpeeled tamarack	Well-house	41	0.44	Splinter 1"x 3"x18"; from end to rail	Sample sound. Slightly decayed in center of tie

Table II.- Description of samples taken from Chicago and Northwestern test track (Cont'd.)

Tie No.	Species	Process used in treatment	No. of ties in treatment	Average absorption	Portion taken as sample	Remarks
891	Peeled hemlock	Well-house	40	0.43	Splinter ½"x 3"x18"; split from end to rail	Tie sound. Sample sound
913	Peeled hemlock	Well-house	40	0.43	Slab 1"x4½"x 36"; entire top section of tie above ground	Under side of sample decayed. Tie badly decayed under sample. Ends sound
1617	Peeled hemlock	Well-house	41	0.52	Splinter 1"x 2"x18"; split from end to rail	Sample sound. Tie sound
1888	Unpeeled hemlock	Well-house	40	0.56	Splinter 1"x 1"x18"; split from end to rail	Sample sound. Tie sound

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duplicate determinations were made. The zinc was determined according to the method devised by Bateman[4] except that in a few cases it was found that the addition of fuming nitric acid reduced the time of digestion and decreased somewhat the amount of acids needed.

The following method of analysis was finally adopted for the chlorine:

Five gms. of sawdust was placed in an iron crucible along with 20 cc. of concentrated caustic soda. This was gently heated with continual stirring on a sand bath until the water had been driven off and the caustic brought to the fusion point. Strict attention must be given it through the heating period; in the early stage of heating it is somewhat liable to spatter while in the latter stage it foams badly and can only be controlled by stirring. The color of the mix is at first dark brown but gradually becomes much lighter and its consistency changes from that of moist meal to a heavy syrup. Beyond this the fusion becomes darker and granular. When this point was reached, 5 gms. of c. p. potassium nitrate was stirred into the fusion and after the glowing had ceased it was removed from the bath and allowed to cool. When cool it was taken up with water, neutralized with nitric acid and filtered. The

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chlorine was then determined in the filtrate by Volhard's method. Blank determinations must be made on the caustic solution and KNO_3 in order to correct for the chlorine which is usually present. Table III gives some idea of the accuracy of the method. In general the agreement with the theoretical value is about as good as can be expected and is sufficiently accurate for the work in hand.

Table III.- Accuracy of method of determining chlorine in treated wood

Amount of wood taken	Chlorine taken	$ZnSO_4$	Found	Found corrected for blank	Difference
gms.	gms.	gms.	gms.		
5.00	0	0	.0226		
5.00	.0725	0	.0948	.0722	.0003
5.00	.0950	0	.1174	.0948	.0002
5.00	0	0	.0298		
5.00	.0337	.5	.0630	.0332	.0005
5.00	.0426	.5	.0716	.0418	.0008
5.00	.1021	.5	.1292	.0994	.0027

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Results of Analyses

The results obtained are given in the following table:[5]

Table IV.- Zinc and chlorine content of section of ties treated with zinc chloride after 7 and 10 years' service

Tie No.	Zinc found by wt	Chlorine found by wt.	Zinc chloride if all chlorine is in form of $ZnCl_2$	Excess zinc by wt.	Zinc present which had been hydrolyzed
	Per cent	Per cent	Per cent	Per cent	Per cent
319					
Sect. I					
A	.425	.110	.211	.324	76.3
B	.422	.083	.160	.345	81.7
C	.437	.043	.088	.397	91.0
D	.167	.032	.062	.137	82.0
E	.341	.028	.054	.313	91.8
F	.424	.028	.054	.396	93.4
Sect. II					
A	.44	.08	.15	.37	84.1
B	.55	.16	.31	.40	72.8
C	.[illegible]2	.05	.10	.37	88.1
D	.41	.028	.05	.36	87.9
E	.67	.067	.13	.61	91.1
F	.37	.089	.17	.29	78.4
200	.487	.074	.142	.419	86.0
313	.375	.070	.134	.311	83.0
486	.427	.070	.134	.363	85.0
527	.451	.060	.115	.396	87.8
657	.540	.094	.181	.453	83.9
752	.461	.094	.181	.374	81.2
891	.497	.106	.204	.399	80.3
913	.430	.068	.131	.367	78.4
1617	.417	.094	.181	.330	79.2
1888	.483	.160	.308	.335	69.4

[5] Thanks are due to Mr. G. G. Town, Assistant Chemist, for about one-half of the analytical data given here.

Table V.- Comparison in method of calculating the zinc chloride content of wood

Tie No.	Specific gravity of sample before analysis	Zinc chloride content if all the zinc were in form of zinc chloride	Zinc chloride content if all the chlorine were in form of zinc chloride
		lbs. per cu. ft.	lbs. per cu. ft.
319			
Sect. I			
A	.535	0.295	0.071
B	.227	0.125	0.022
C	.212	0.123	0.222
D	.565	0.123	0.032
E	.636[a]	0.281	0.022
F	.258	0.140	0.008
Sect. II			
A	.580	0.316	0.074
B	.622	0.445	0.116
C	.395	0.225	0.042
D	.482	0.366	0.082
E	.500	0.436	0.080
F	.600	0.320	0.039
200	0.310	0.191	0.027
313	0.386	0.191	0.033
486	0.553	0.320	0.047
527	.440	0.256	0.031
657	0.521	0.367	0.057
752	0.500	0.302	0.056
891	0.352	0.228	0.045
913	0.341	0.190	0.021
1617	0.314	0.169	0.038
1888	0.350	0.223	0.069

[a] This section contained a large knot.

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It is the usual practice in the wood preservation industry to refer to the amount of zinc in terms of pounds of dry zinc chloride per cubic foot. The results of the analyses have therefore been calculated to terms of pounds zinc chloride per cubic foot (a) when the amount of zinc found was taken as a basis, (b) when the amount of chlorine found was taken as a basis.

Discussion

It is very evident from the data shown that in actual practice the chlorine disappears from the wood much faster than the zinc as would be expected from the preceding theoretical discussion. Unfortunately we have no way of calculating the amount of loss by leaching because we have no data upon which to base the original amount in the samples under consideration.

Particular attention is directed to section 2, pieces D, E, and F, of tie No. 319, as shown in the diagrammatic sketch Plate I. These pieces contained the zinc equivalent of 0.366, 0.436, and 0.320 pounds of zinc chloride per cubic foot and are badly decayed. It is usually considered that .3 pounds of zinc chloride per cubic foot is the killing point of timber destroying fungi. In these three pieces at least there is still left after seven years' service enough zinc which if it were in the form of zinc chloride would prevent decay. If, however, we compare the

amount of zinc chloride as calculated from the chlorine present, we find that in general the sound portions have the most chlorine and the pieces marked badly decayed but hard have not quite as much chlorine but contain more than the pieces marked badly decayed - punky. In other words there seems to be a general relation between the chlorine content and degree of decay. The ten samples taken from the Janesville track simply confirm the finding of tie No. 319. The data available is not sufficient to draw any conclusions on the relative permanence of zinc chloride in ties treated by the Burnett and Wellhouse processes, nor can any conclusion be drawn as to the relative leaching from the two species used. Slightly less of the residual zinc was in a hydrolyzed condition in the ties which were unpeeled before treatment than others of the same species and treatment but peeled before treatment. The difference is, however, small; the variations being less than the variations obtained from the different locations in the same tie. It may also be due to differences in absorption of zinc, the unpeeled ties taking up more than peeled ties of the same species under the same treatment.

Conclusions

The following conclusions can be drawn from the work:

1. In the leaching of zinc chloride from wood the

chlorine leaches faster than the zinc, part of which is left behind as an insoluble basic chloride. This would seem to indicate that the chlorine plays a very important part in the preservative and that if the zinc does not have its proper amount of acid radical it loses its preserving power. In other words, as long as the zinc remains soluble it is toxic but as soon as the insoluble basic chlorides are formed, the zinc so combined has but little or no toxic action.

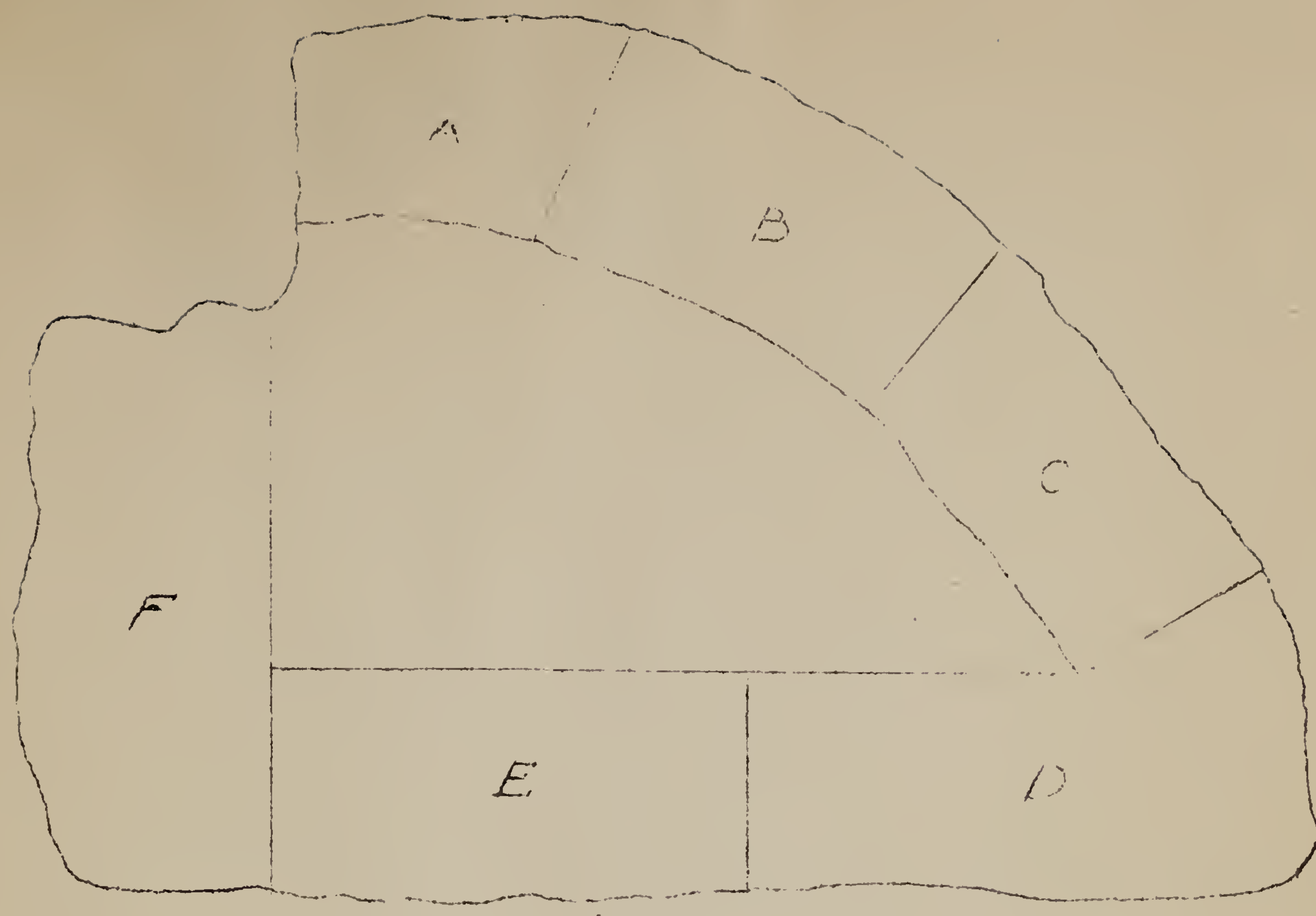
2. The amount of each component leached can be calculated with fair accuracy from the diffusion constants of hychloric acid and zinc chloride and the amount of each component present in the mixture.

3. From the above it follows that the relative rate of leaching of any other salt from wood probably can be calculated if we know the amount injected and the diffusion constant of the salt.

4. The leaching of zinc chloride from wood in actual practice is similar to, if not identical with, the leaching of the same salt under laboratory conditions.

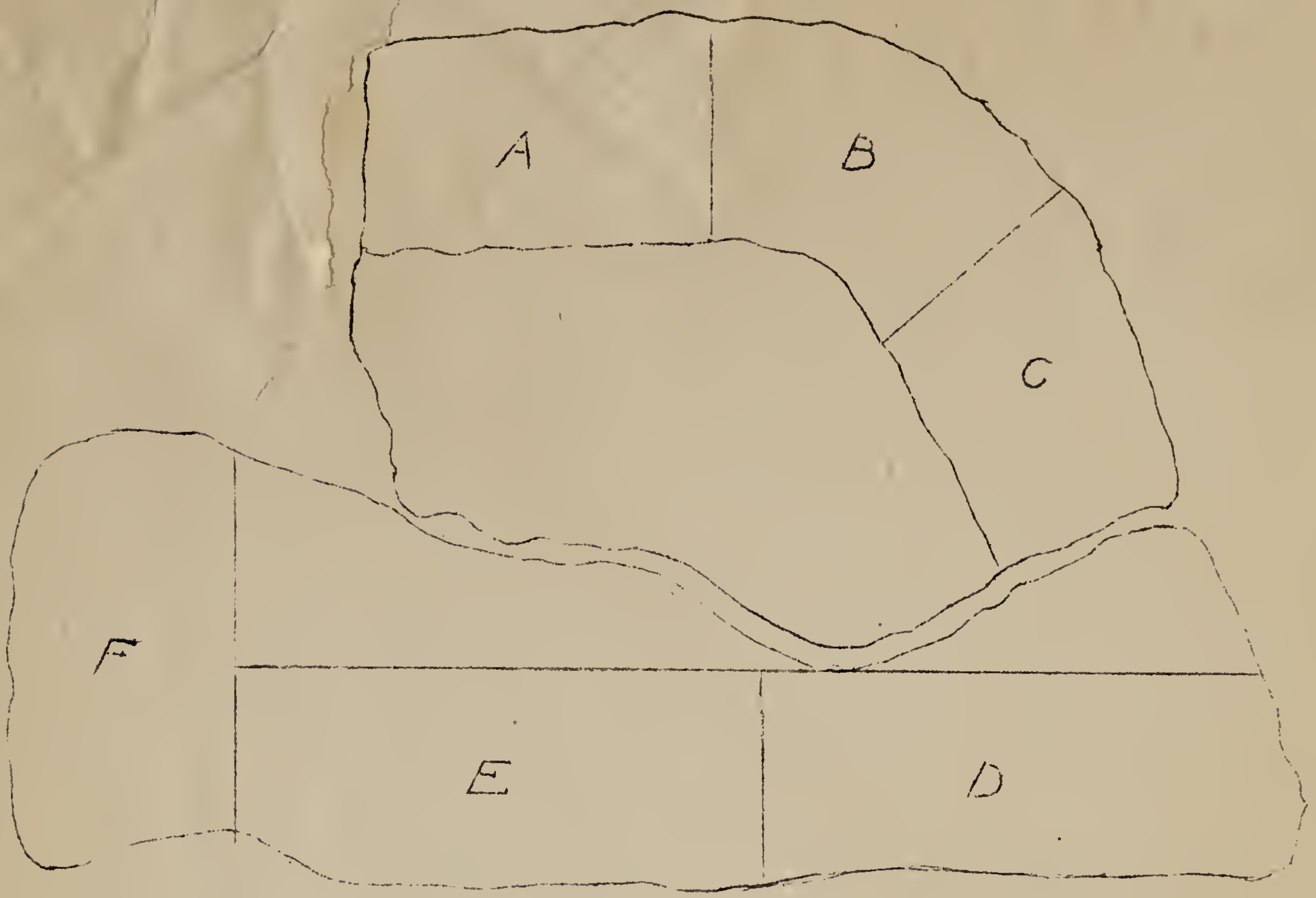
5. The presence of comparatively large amounts of zinc in treated material does not insure that the wood is protected against rot unless a sufficient amount of acid radical be also shown to be present.

6. The insoluble basic chlorides of zinc have little or no toxic value.



Section 1 - Tie No. 319

Piece No.	Condition of sample analyzed	Content of zinc chloride equivalent to Zinc lbs. per cu.ft.	Chlorine lbs. per cu.ft.
A	Apparently sound	.295	.071
B	" "	.125	.022
C	Badly decayed - punky	.123	.022
D	Badly decayed but hard fruiting bodies of fungus on bottom	.123	.032
E	Badly decayed but hard fruiting bodies of fungus on bottom	0.281	0.022
F	Badly decayed - punky	.140	.008



Section 2 - Tie No. 319

Piece No.	Condition of sample analyzed	Content of zinc chloride equivalent to	
		Zinc lbs. per cu. ft	Chlorine lbs. per cu.ft.
A	Apparently sound	0.316	0.074
B	" "	.445	.116
C	Partly sound - rest punky	.225	.042
D	Badly decayed - one half punky - rest sound	.366	.082
E	Badly decayed - one half punky - rest sound	.436	.080
F	Badly decayed but hard	.320	.039